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Metallic Reflection from Molecular Crystals*

BASIL G. ANEX† AND WILLIAM T. SIMPSON

University of Washington, Seattle, Washington

I. INTRODUCTION

ACCORDING to the Drude theory of metals, the index of refraction varies with frequency in a simple manner provided the period is much shorter than the collision-determined relaxation time. Then

$$n^2-1=-\omega_p^2/\omega^2,$$

where ω_p^2 is the plasma frequency squared,

$$\omega_p^2=4\pi(Nf)e^2/m,$$

and Nf is the number of optical electrons per cm³. If n is real, the reflectance for a dielectric at normal incidence obeys the simple Fresnel formula[1]

$$R=(n-1)^2/(n+1)^2.$$

Thus, when ω decreases until

$$\omega^2=\omega_p^2,$$

we have n^2 going to zero (and then becoming imaginary) with the result that R goes to unity and remains there. For simple metals the theory is in particularly good agreement in that there is quite a sudden rise in R to almost unity as ω approaches ω_p.

In this paper it is shown how a very similar phenomenon occurs with molecular crystals. The individual "molecules"—dye cations in the case mainly considered here—are effectively isolated from one another just as in all molecular crystals. No tangible exchange of electrons from one molecule to another takes place in the excited crystal levels, even though something closely akin to metallic reflectivity occurs.

What happens is that for some dyes ω_p is reached at such a high frequency that the pertinent relaxation phenomenon cannot occur. The relaxation time in the case of dye cations is the reciprocal of the frequency of the strong first electronic transition. The reason is that, according to a correspondence principle argument, this time is the time for the optical electrons to go from one end of the dye molecule to the other and back while the particular molecule is undergoing transition: $\tau=\omega_0^{-1}=\hbar/\Delta E$. This correspondence principle model gives a simple way of seeing how the Drude theory applies. At high frequencies the electric vector of the light (and thus also each following electron) reverses direction so rapidly that the electrons do not have their simply periodic to-and-fro motion interrupted by collisions with the potential walls at the ends of the dye molecule. The attendant **P** vector generated inside the molecular crystal considered as a dielectric is accordingly virtually the same as the **P** vector in a material for which the electrons are free, namely, a metal.

An example of metallic reflection in a molecular crystal is afforded by the substance, 1,5-bis-(dimethylamino) pentamethinium perchlorate, henceforth referred to as BDP,

$$\mathrm{Me_2\overset{+}{N}{=}CH{-}CH{=}CH{-}CH{=}CH{-}NMe_2,\quad ClO_4^-}.$$

The reflection spectrum for this substance is shown in Fig. 1. Focusing on principal direction 1, the first thing that one notices is the sudden onset of very high reflectivity going from the high-frequency region. This reflectivity begins at a frequency remote from the single molecule (solution) absorption (dot-dashed curve) and continues high until it suddenly changes at a point somewhat to the red of the solution absorption. All this is in substantial agreement with what is predicted by the Drude theory.

By keeping to the same simple picture we can even derive a criterion for the occurrence of the phenomenon of metallic reflection. According to our model, we must have

$$\omega_p>\omega_0$$

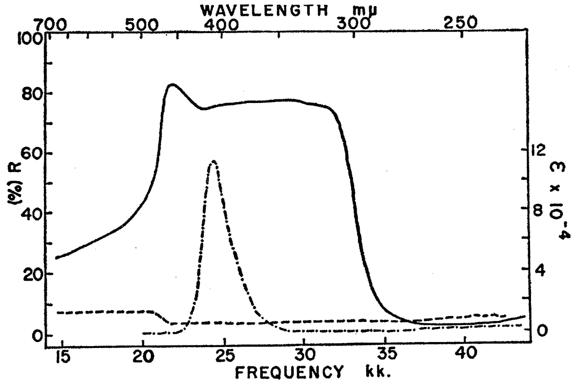

FIG. 1. Crystal reflection spectra for face 1 of 1,5-bis-(dimethylamino)pentamethinium perchlorate obtained with light polarized along principal directions 1 (——) and 2 (- - -); and the absorption spectrum of a water solution of the same compound (-·-·).

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† National Science Predoctoral Fellow, 1955–58. Present address: Department of Chemistry, Indiana University, Bloomington, Indiana.

[1] If we wish to consider absorption, we use a complex index of refraction, in which case

$$R=[(n-1)^2+k^2]/[(n+1)^2+k^2],$$

where now n and k are the real and imaginary parts.

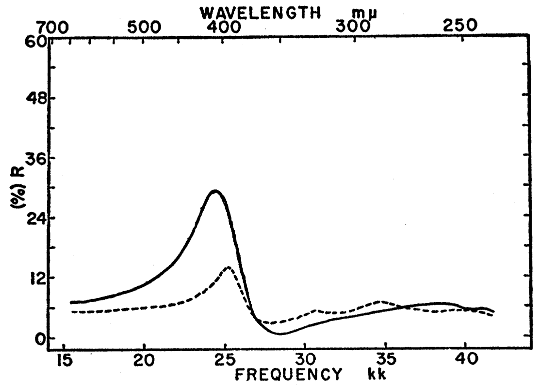

FIG. 2. Crystal reflection spectra for one face of auramine perchlorate obtained with light polarized along the principal directions.

where (at the present level of explanation) ω_0 is the frequency found in the solution spectrum. This shows that Nf must be high, which represents two conflicting requirements. N is the number of molecules/cm^3 and is inversely proportional to dye length l. The oscillator strength f is proportional to the transition-moment length squared times the frequency, giving an l^2 dependence times an l^{-1} dependence. All together then, we have no l dependence for Nf. To have ω_p high we need to have a favorable projection of the transition moment on a given principal direction of the crystal face being viewed and we need to have the space inside the crystal given over to the production of color. The substance BDP is compact but not ideal because the perchlorate ions lower N without raising f. As it develops, for BDP the orientation is very favorable.

Application of the criterion to BDP requires the computation of ω_p, which turns out to be 5.7×10^{15} (circular frequency). The corresponding resonance comes at 4.6×10^{15}, so the criterion $\omega_p>\omega_0$ succeeds. For the yellow dye auramine perchlorate, there is incipient metallic reflection, but not for the face shown in Fig. 2. Consideration of the geometry of auramine along with the N value and single molecule intensity shows that, according to our criterion, metalic reflection ought not be expected, and it is seen in Fig. 2 that the reflectance is conventional—much like the derivative of an absorption curve.

Naturally one ought not expect the Drude theory to be the whole story, and indeed it is found that a somewhat different appearance criterion is more fundamental. Also, the dispersion theory with the Lorentz-Lorenz correction turns out to be applicable, a fact which is in conflict with our use of the Drude theory (which is related to the Sellmeier formula). As a consequence, it is better to take for τ^{-1} a frequency derived from the single-molecule frequency after consideration of the internal field.

A physical picture of the approach to high reflectivity (from the high-frequency side) may be obtained from dispersion theory. When $\omega>\omega_p$, the material is a dielectric, but as $\omega\rightarrow\omega_p$, the wavelength inside the dielectric gets longer and longer. Finally, when $\omega=\omega_p$, the light incident on a physical surface suddenly is coupled simultaneously to all the optical electrons inside the dielectric (infinite phase velocity). At this point the impedance for the currents transverse to the propagation vector becomes infinite and no light can penetrate. This in turn fixes the boundary conditions for the incident light so that the incident radiation becomes a standing wave, which is equivalent to two running waves of equal intensities, and hence total reflection.

Before considering theoretical aspects in greater detail, we turn to the technique for obtaining a reflection spectrum, a consideration of the peripheral experiments, and the results.[2]

II. EXPERIMENTAL AND RESULTS

The spectrophotometer used consists of a monochromator, beam splitter, microscope objective, target, polarizer, and detector. The light from the monochromator passes through the objective, is reflected from the target at normal incidence, goes back through the objective, and is directed towards the analyzing system by the beam splitter. The target is alternately a crystal face or a standard mirror, the two being mounted on a sliding stage so that the detector can be set full scale at a given wavelength with the mirror in position and then the crystal moved into position for a reflectance reading. The stage was kinematically designed, with the result that reproducibility may be obtained even using 53× magnification (perhaps it would be better to say demagnification). The objectives are interchangeable, though mainly a Bausch and Lomb 53× reflecting-refracting objective was used (Polaroid grey design V, focal length 2.8 mm, numerical aperture 0.72). The standard mirror is aluminum and absolute reflectance was calculated using the data of Schulz and of Strong for aluminum.[3] The polarizer used in the uv was a Glan-Thompson, with elements soaked apart and a drop of glycerine used at the interface. The beam splitter is a quartz flat, homogeneously aluminized for ca 50% transmission.

The present practice in this Laboratory is to use a quartz microscope objective (which necessitates refocusing as the wavelength is varied) together with a Glan-type prism with air interface.[4] By using these components we are able to extend the uv range to 200–210 mμ.

The reflection spectrum of gold was determined as a

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[2] J. Weigl [J. Chem. Phys. 24, 577 (1956) and J. Mol. Spectroscopy 1, 216 (1957)] made earlier measurements of the reflectance of thin films of dyes. He noticed an undue broadening associated with strong absorptions which he interpreted as a strong coupling phenomenon in the sense of footnote 8.

[3] L. G. Schulz, J. Opt. Soc. Am. 44, 357, 362 (1944); J. Strong, *Procedures in Experimental Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1938).

[4] Item 4B, catalog of Karl Lambrecht, 4318 N. Lincoln Avenue, Chicago 18, Illinois.

check on design and procedure, and Schulz' data was matched satisfactorily.

In addition to reflection measurements, miscellaneous experiments were carried out: recrystallization of samples to check initial purity and possible contamination through photodecomposition, determination of crystal density, quantitative solution absorption to find the single-molecule frequencies and intensities, and examination of crystal morphology.

We next consider the results. The substance predominant in the present investigation is BDP. Considerable work was also done on auramine perchlorate, but these results are mentioned only in passing. (A report on auramine is being prepared for publication elsewhere.) A typical spectrum for auramine perchlorate is shown in Fig. 2, where the reflection is recorded for light polarized along each principal direction. The abrupt rise and fall of the reflectance for one of the principal directions at ca 400 mμ come from a resonance in the dispersion formula associated with the strong electronic transition which gives auramine its yellow color. Spectral features at 330 and again at 290 mμ differ in that the principal direction of higher reflectivity has switched. This kind of observation makes it possible to deduce relative polarizations in the single molecules (or ions), most easily when there is only one molecule per unit cell, but also in many other cases of less favorable symmetry.[5]

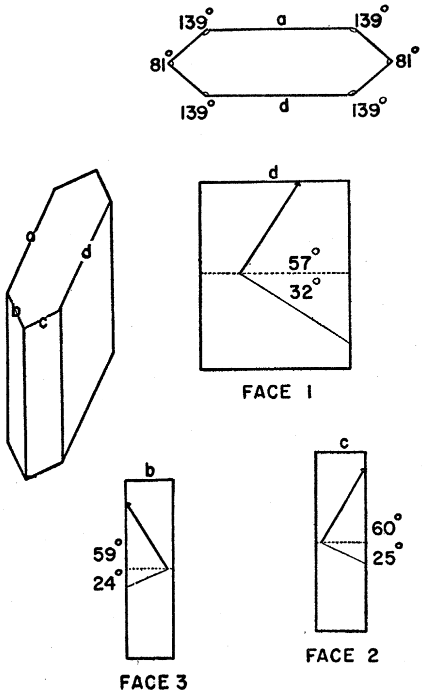

Fig. 3. Crystal morphology and principal directions for 1,5-bis-(dimethylamino)pentamethinium perchlorate. The faces and principal directions in a given face have been arbitrarily designated by number. In each case, the upper angle refers to principal direction 1, while the lower angle refers to principal direction 2.

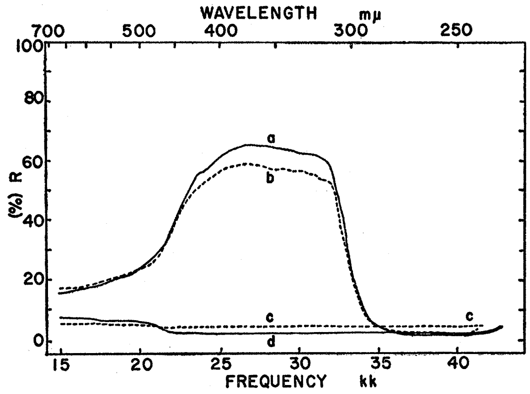

Fig. 4. Crystal reflection spectra of faces 2 (——) and 3 (- - -) of 1,5-bis-(dimethylamino)pentamethinium perchlorate. For each face, the curve which shows the metallic reflection peak (*a*; *b*) is that obtained with light polarized along principal direction 1, and the relatively structureless curve (*c*; *d*) is that obtained with light polarized along principal direction 2.

Turning now to the results for BDP, we show the reflection spectra on each of three faces, the positions of the faces being first recorded in Fig. 3. Figure 1 has the spectrum on what was considered the "main face" or face 1, plotted along with the single-molecule absorption curve. Figure 4 has the reflectance on faces 2 and 3. The main face was the largest and most tractable and, incidentally, has the most spectacularly atypical reflection spectrum. Work on the other faces was difficult because they are narrow and required the use of the full microcapabilities of the spectrophotometer. Keeping in mind the experimental difficulties, it is concluded that faces 2 and 3 have the same reflection spectra. This work is mainly important in that lacking a crystal structure, we can infer a great deal about how the single molecules (cations) are lined up, which information is needed in connection with later interpretations.

The crystal of BDP showed a fluorescence which, according to visual determinations, using a hand spectroscope, went from 500–550 mμ, with a maximum at about 525. This fluorescence is probably the same or nearly the same as the single-molecule and is independent of exciting wavelength from 430 to 367 as nearly as could be seen. Strangely enough, no sharp cutoff could be detected (photometrically) in the fluorescence corresponding to the abrupt change in reflectance at 315 nor could a sudden increase in transmittance be found.

The density of BDP was found to be 1.311±0.001 g/cm^3.

The single-molecule absorption at 409 mμ (24.4 kk) has an integrated intensity corresponding to a transition moment length $|y|$ of 2.04 A. A one-dimensional oscillator strength of 3.31 is computed from this length according to

$$f=(2m\omega/\hbar)|y|^2.$$

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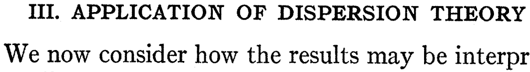
[5] A. Bree and L. E. Lyons, J. Chem. Soc. (**1956**) 2662.

This one-dimensional oscillator strength is the quantity occurring in the usual graft of quantum theory onto classical dispersion theory. It is three times higher than the one used in atomic spectroscopy wherein one compares intensities with ideal intensities for an isotropic harmonic oscillator in its ground state. The theoretical maximum one-dimensional oscillar strength is sometimes mistakenly considered to be two on an orbital picture (two electrons in the originating orbital). Actually, a strength as high as 3.31 as observed here is not anomalous because the Pauli principle makes the originating orbital have nodes: three, going down the axis for the pentamethinium dye. What should be compared then is the intensity of a harmonic oscillator also with three nodes, considering the dependence of the harmonic oscillator intensity on quantum number. We should therefore compare the observed $f=3.31$ with a maximum of eight, including the factor of two because the originating orbital is doubly occupied.

The transition moment lengths and f values for the weak absorptions at 255 and 225 mμ are 0.34 and 0.32 A, corresponding to f values each of 0.15.

The half-width of the single-molecule absorption at 409 mμ was found to be 0.374×10^{15} (units of ω, the circular frequency). The widths of the reflection bands may have to be characterized differently than the widths of absorption bands owing to the way the reflection coefficient slowly falls off at higher wavelengths in accordance with the dispersion formula and the way other transitions affect the reflection. Such characterization is of necessity somewhat arbitrary. The difference between the ω^2 values at the onset and cessation of strong reflection is to be used in the theoretical analysis that follows. For face 1 of BDP, this ω^2 is estimated to be 19.4×10^{30}. The corresponding difference in the ω values taken at the same points is 2.98×10^{15}. (This width should be compared to the single-molecule width of 0.374×10^{15}.)

Several substances other than BDP which show metallic reflectivity have been examined. A particularly interesting one, forming a true molecular crystal, is the nonionic molecule 5-*N*-methylanilino-2,4-pentadienal. It is a dye vinylogous to an amide,



The reflection spectrum is shown in Fig. 5. There is not a simple rise on the long wavelength side, but a rise and fall, then a secondary rise coming at ca 340 mμ. The single-molecule absorption (in methanol) for this dye peaks at 380 mμ.

III. APPLICATION OF DISPERSION THEORY

We now consider how the results may be interpreted according to classical dispersion theory modified to contain quantum oscillator strengths. The point of view is first a formal one, where we try to fit the observed reflection spectrum, and thus verify the single-molecule constants. When we have achieved a reasonable fit, we return (Sec. IV) to the physical interpretation, which involves the meaning of the damping constant.

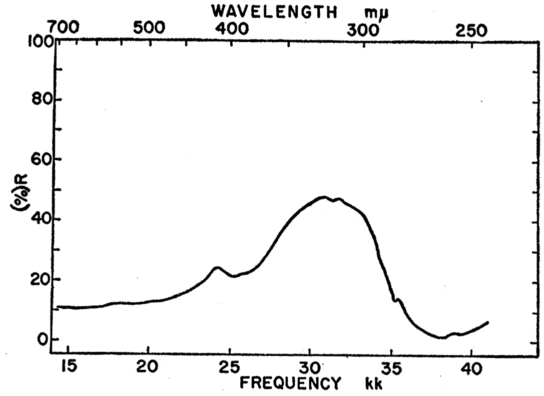


FIG. 5. Crystal reflection spectrum for one face of 5-*N*-methylanilino-2,4-pentadienal obtained with light polarized along one of the principal directions.

The single-molecule constants obviously cannot be used to predict the reflectivity of any one crystal face without prior knowledge of the crystal structure. In fact, the transition moment could have any projected value whatsoever. It turns out that, for BDP, having the reflection data on three faces provides enough structural information effectively to fix the molecular orientation. The reflectance on all three faces has the characteristic that the molecular transition moments project onto a single principal direction (the dashed curves in Figs. 1 and 4 are taken as showing essentially no reflectance related to the 409 mμ transition). Thus the molecular axis along which the transition is polarized in a single molecule has only one orientation in the crystal.

If the trial assumption is made that this orientation is unconditionally parallel to face 1, and therefore 57° from horizontal, as recorded in Fig. 3 for principal direction 1 of face 1, one can predict the direction of maximum reflectance in faces 2 and 3. The prediction is that the direction be the same in both faces, 58° from horizontal. The predicted angles and the prediction of equality for the two faces are found to hold within experimental error. The trial assumption may now be considered as correct, and as furnishing a structural model. According to the model, the projected transition moment squared on faces 2 and 3 is 0.87 times the maximum. Thus the ratio of f values as between face 1 and face 2 and 3 should also be 0.87. As we shall see, the f or $\omega_p{}^2$ value approximately determines the width (not the height, as one might expect) of the region of high reflection. According to how the width is characterized we observe a ratio of widths squared as between face 1 and the other two faces in the range 0.83 to 0.93, in practical agreement with the structural model. We now have the result that the f value inferred from face 1 ought to be compared directly with the molecular f value without any intervening trigonometric factor.

The next step is to cast the dispersion theory into a usable form. The ever present difficulty—lack of infor-

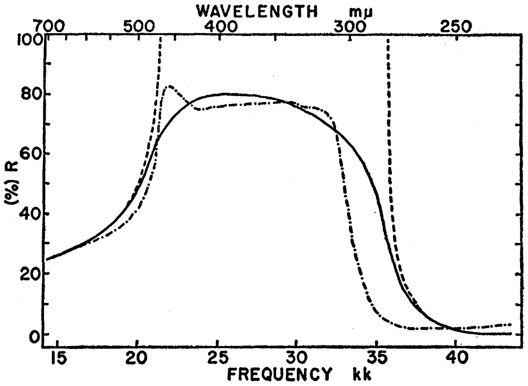


FIG. 6. Theoretical reflection curves for 1,5-bis-(dimethylamino)pentamethinium perchlorate with $\omega_p^2=32.9\times10^{30}$ and $\gamma=0$ (– – –), and $\gamma=0.361\times10^{15}$ (——). The experimental reflection spectrum for principal direction 1 of face 1 is shown for reference (–·–·).

mation about higher transitions—is not a serious one here because of the strength of the transition at 409 mμ and the wide gap before additional transitions occur (the next transitions are weak and do not come until 255 and 225 mμ). Thus we write the dispersion formula so that the influence of the higher transitions may be taken, in first approximation, as constant

$$\frac{n^2-1}{n^2+2}=\frac{\omega_p^2/3}{\omega_0^2-\omega^2+i\gamma\omega}+G.$$

There are four constants in this formula to be evaluated from the reflection spectrum in Fig. 1. Apart from G, one can obtain ω_p^2 and hence the single molecule f; the damping constant γ, which turns out to be the single-molecule vibronic band half-width; and the explicit resonance ω_0, which, in simple applications of the dispersion theory, is the single-molecule frequency.[6]

Considerable labor was put into looking for a best fit. The procedure followed was first to work on the long wavelength dielectric region. Here one can go from R values to values of $(n^2-1)/(n^2+1)$ by using the simple Fresnel formula. Then with $\gamma=0$, one can find pairs of G, ω_0 which fit the data reasonably well; one pair for each ω_p value. The dashed curve in Fig. 6 shows what is found if $\omega_p^2=32.9\times10^{30}$, which is the value obtained by using

$$\omega_p^2=4\pi Nfe^2/m$$

and substituting the observed crystal density for N and the observed single-molecule value $f=3.31$. For this case, $G=0.25$ and $\omega_0^2=30.7\times10^{30}$.

A G value of 0.25 is reasonable in that it implies a residual index of refraction $n=1.4$, with a corresponding reflectance of 0.03. The ω_0 value corresponds to absorption at 340 mμ, which obviously does not coincide with the single-molecule value of 409 mμ. As will eventually be shown, when the straight Lorentz-Lorenz formula is used, ω_0 very nearly has to be taken as the single-molecule frequency corrected for the short-range electrostatic resonance interaction (V_1 in the notation of Sec. V). That there is a blue shift is not unexpected for long molecules because their sidewise repulsive interaction occurs at a smaller distance than their end-for-end interaction, which is attractive.

The dashed curve in Fig. 6 is too wide. The effect of allowing G to increase slowly as ω increases is to move the high-frequency side of the metallic reflection region to longer wavelengths, thus causing a narrowing. This narrowing is brought about even more efficiently by putting in the high-energy transition explicitly. Quantiatative consideration of these effects shows that the narrowing to be expected might well bring the dashed curve into reasonable coincidence with the experimental curve. Further consideration indicates that, in any case, the best fitting ω_p^2 value is greater than 26×10^{-10}, all of which implies a wavelength (corresponding to ω_0) less than 350 mμ.

All attempts to fit the data using a formula of the Sellmeier type,

$$n^2-1=\sum_j\frac{(\omega_p^2)_j}{\omega_{0j}^2-\omega^2+i\gamma_j\omega},$$

failed. This is at first sight surprising because a one-term Lorentz-Lorenz formula can be recast into the Sellmeier form if the explicit resonance ω_0^2 is modified. The many-term Lorentz-Lorenz formula as approximated by the G formula above cannot, however, be transformed into a formula of the Sellmeier type, with an additive term representing the higher transitions. Instead, what one finds is

$$n^2-1=\frac{\omega_p^2+3G(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)-\frac{1}{3}[\omega_p^2+3G(\omega_0^2-\omega^2)]}.$$

Up until now we have been leaving the damping constant out of consideration. When it is introduced, the n values become complex and the generalized Fresnel formulas have to be used to compute reflectance. The effect of varying γ is essentially to vary the height of the metallic reflectance. Thus, a somewhat different value of γ could be derived from the curves for faces 2 and 3. The best fit value for face 1 is $\gamma=0.36\times10^{15}$, leading to the solid curve in Fig. 6. This is to be compared with the half-width of the solution absorption curve, 0.37×10^{15}, and the two values are amazingly close. We postpone interpreting this result until Sec. IV.

If we take $G=0$, $\gamma=0$, we can readily obtain a formula of the Sellmeier type,

$$n^2-1=\frac{\omega_p^2}{(\omega_0^2-\omega_p^2/3)-\omega^2},$$

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[6] There is a certain amount of interaction between f and ω_0 in that to calculate f from ω_p^2 one has to decide whether to use ω_0 or the single-molecule frequency. This kind of ambiguity occurs typically when second-order perturbation theory is being used.

which has an explicit resonance at the low-frequency boundary (the index of refraction becomes infinite),

$$\omega_-^2=\omega_0^2-\omega_p^2/3.$$

Defining a function of the index of refraction which puts emphasis on wavelength in the medium instead of velocity

$$p^2=1/n^2,$$

we can change the appearance of the basic formula,

$$p^2-1=\frac{-\omega_p^2}{(\omega_0^2+2\omega_p^2/3)-\omega^2}.$$

This has an explicit resonance at the high-frequency boundary (the wavelength becomes infinite),

$$\omega_+^2=\omega_0^2+2\omega_p^2/3.$$

Accordingly, we may define a width[7]

$$\omega_+^2-\omega_-^2=\omega_p^2.$$

This shows why ω_p^2 is so important in determining the width in an actual case. An interesting consequence is that when $G=0$, the conventional explicit resonance ω_0^2 comes $\frac{2}{3}$ of the way from the short-wavelength boundary of the metallic reflection region. Having the three equations: for $(n^2-1)/(n^2+2)$, for n^2-1, and for p^2-1, each with its own different explicit resonance frequency within the region makes one think that all frequencies within the region are on a more or less equal footing. Perhaps, then, any single frequency from ω_+ to ω_- can be considered as a stationary state reached in an allowed crystal transition. This point of view is explored further in the final section.

IV. OCCURRENCE CRITERION

We use the $G=0$ results for the width, avoiding unnecessary complication. Then

$$\omega_p^2=(\omega_++\omega_-)(\omega_+-\omega_-)\approx 2\omega_0(\omega_+-\omega_-)$$

so that with $\omega_+-\omega_-=\Delta\omega$,

$$\Delta\omega\approx\omega_p^2/2\omega_0.$$

We now take as the criterion for the appearance of metallic reflection that the width $\Delta\omega$ must be sufficient to cause the normal dispersion curve to change in appearance noticeably. The normal curve has a width governed by γ, which is the reciprocal lifetime of the electronic excitation in the dielectric. The fundamental inequality is therefore

$$\omega_p^2/2\omega_0>\gamma.$$

The reverse inequality implies the absence of an effect.

The simple inequality $\omega_p>\omega_0$ obtained in connection with the explanation according to the Drude theory is not really the same thing. Thus, at the point of balance the fundamental criterion is

$$\omega_p^2/2\omega_0\approx\gamma\approx\omega_+-\omega_-$$

so that

$$\omega_p\approx[2(\omega_+-\omega_-)/\omega_p]\omega_0.$$

By reason of the connection between ω_p^2 and width squared, the quantity in square brackets is of the order of unity. Thus, roughly, at the point of balance, we have the simpler relation

$$\omega_p\sim\omega_0.$$

This comparison changes in the right direction on either side of the point of balance and so could have partial success.

Returning to the fundamental inequality, we now transform back to the defining quantities to facilitate interpretation. Combining

$$\omega_p^2/2\omega_0=(4\pi Nfe^2/m)/2\omega_0$$

with

$$f=2m\omega_0|y|^2/\hbar$$

(where $e|y|$ is the magnitude of the transition moment, m_y) gives

$$(4\pi Ne^2|y|^2)/\hbar>\gamma.$$

But $1/N$ is virtually the cube of the nearest-neighbor distance D,

$$(1/N)\approx D^3,$$

so that we have the result (energy units)

$$4\pi m_y^2/D^3>\hbar\gamma.$$

This bears a striking resemblance to the coupling inequality[8]

$$2V>\Delta$$

in which it is suggested that one compare $2V$, the dimer split for a pair of neighboring molecules disposed so as to correspond to the strongest interaction occurring in the crystal, with Δ, the single-molecule half-width, as taken from the solution spectrum. The quantity $4\pi m_y^2/D^3$ is virtually this suggested dimer split; and, as pointed out in Sec. III, γ is found empirically to be equal within experimental error to the single-molecule half-width (as determined experimentally from the solution spectrum). It is evident that metallic reflection is a strong coupling phenomenon. In fact, one immediately thinks of turning the argument around and using $\hbar\omega_p^2/2\omega_0$ for the electronic bandwidth of a crystal in place of the somewhat clumsy dimer split $2V$.

The physical meaning of the electronic bandwidth is discussed in Sec. V. The physical meaning of our finding that empirically $\gamma=\Delta/\hbar$ for face 1 is that the relaxation

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[7] If it is assumed that the higher transitions can be accounted for by using a constant G, this becomes

$$\omega_+^2-\omega_-^2=\omega_p^2(1+G-2G^2)^{-1}$$

or with $G=0.25$ as determined in the foregoing, $\omega_+^2-\omega_-^2\approx 0.9\omega_p^2$.

[8] W. T. Simpson and D. L. Peterson, J. Chem. Phys. **26**, 588 (1957).

phenomenon occurring is the trapping of the crystal electronic excitation on a single molecule. This is followed by other processes, e.g., fluorescence, which, however, do not influence γ. The trapping occurs because the force constants and equilibrium configuration change going from the ground to the excited state of an isolated single molecule. Electronic excitation in the crystal can pass freely from one molecule to another so long as the internuclear configuration remains the same as for the ground state. Once the nuclei start to oscillate as a wave packet, transition has occurred from the crystal level. The width Δ is not to be confused with the width of a single vibronic level in the single molecule spectrum, this latter width being a measure of the vibrational cascade probability, fluorescence probability, etc.

It may happen that more efficient trapping than implied by Δ can occur through the intervention of coupled variations involving more than one molecule; in fact, the lower reflectance on faces 2 and 3 (higher γ) may be a sign that such a trapping process is occurring.

Figure 6 shows that the dispersion theory fails to reproduce the observed structure. The interpretation of the metallic reflection region as a block of levels makes it possible to see how structure might occur. We can imagine that the relaxation process is essentially as described previously for face 1 provided the crystal energy is greater than the single-molecule energy. This applies to the part of the reflection for BDP on the high-frequency side of 409 mμ (see Fig. 1). If the crystal energy is lower than the single-molecule energy, it may not be possible for trapping of the excitation energy to occur exactly as pictured in the preceding. This may be the explanation for the unusual appearance —in the case of face 1—on the long-wavelength side of 409 mμ. The explanation is supported by work with other substances showing metallic reflection. For example, the curve for 5-*N*-methylanilino-2,4-pentadienal (Fig. 5) shows a similar change at ca 380 mμ, which is the peak of the solution absorption for this substance. At first thought it is surprising that the single-molecule fluorescence could be observed upon excitation with light at $\lambda > 409$ mμ for BDP, but at room temperature the Boltzmann factor is appreciable for populating the single-molecule state from a crystal level corresponding, say, to $\lambda = 470$ mμ.

In summary, the dispersion theory explains metallic reflection from molecular crystals reasonably well. The reflection data can be worked up to give the position, intensity, and width for a single-molecule transition—though there are reservations. The position may be shifted by an electrostatic perturbation, the intensity is indeterminate until the orientation of the single-molecule moments is known, and the single-molecule vibronic half-width as deduced from γ may be too large owing to the possibility that trapping need not occur at a single molecule.

As we have seen, the theory can be recast into a form which puts the explicit resonance at different places in the region of high reflectivity, suggesting that we may be dealing with a block of allowed crystal transitions. This view is reinforced by the appearance of structure and the promise, if not success, of an explanation involving different crystal levels each with its own damping factor. We therefore attempt a further development of the block of levels idea.

V. QUANTUM THEORY

The theory developed in this section is patterned after the conventional nonrelativistic calculation of the electrostatic perturbation for molecules in weak interaction. The essential new point is that not only the Coulombic interaction has to be considered but also the field radiated by the accelerations occurring at the single molecules. To see that the accumulated effect of this radiation may be appreciable, we make a qualitative comparison with the static part.

The interaction energy is proportional to the field at a single molecule. For the static contribution, this field is

$$E_{\text{stat}} \sim m_y / r^3,$$

where m_y is a transition moment on a neighboring molecule a distance r away. Integrating over all neighbors gives an effect

$$\sim m_y / D^3,$$

where D is a nearest-neighbor distance.

The radiation contribution drops off slowly, as r^{-1},

$$E_{\text{rad}} \sim e\dot{v} / c^2 r.$$

The effect of considering retardation is to collect many contributions like the preceding at a representative distance $\lambda\!\!\!^{-} = c/\omega_0$. Because the motion is harmonic, we may replace $e\dot{v}$ by $m_y \omega^2$, giving the field from a single-neighboring molecule:

$$E_{\text{rad}} \sim m_y \omega^2 / c^2 \lambda\!\!\!^{-} \sim m_y / \lambda\!\!\!^{-3}.$$

If the integrated result is to be comparable to the static contribution, the integration must introduce a factor $\lambda\!\!\!^{-3}/D^3$, which is the number of molecules in a cube $\lambda\!\!\!^{-}$ on a side. This is exactly the right order of magnitude if retardation is taken into account, a fact which encourages one to explore a more formal approach.

The theory presented here is less sophisticated than recent field theoretical treatments.[9] It is felt to be of interest anyway, because it is in a form which makes a connection between rigorous classical dispersion theory and the widely employed hybrid in which quantum mechanics is used for the molecules but not for the radiation. Also, the present theory is directed particularly towards an understanding of the metallic reflection phenomenon.

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[9] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958); S. I. Pekar, J. Exp. Theoret. Phys. (U.S.S.R.) **36**, 451 (1959), p. 314 of translation.

We consider that the radiation is sufficiently dilute so that solving the problem for one unit of excitation in the molecular crystal presents the essential features correctly. Also, we assume strong coupling.[8] The wave function for each member of the block of levels is a sum of products with a ϕ for each molecule

$$\psi_s = \cdots \phi_r \phi_s{}^{\dagger} \phi_t \cdots, \quad \psi = (\nu)^{-\frac{1}{2}} \sum_{s=1}^{\nu} c_s \psi_s.$$

The location of the excitation is given by the dagger, and ν is the number of molecules. The coefficients c_s for a plane wave being propagated along the z axis vary as

$$e^{ikz(s)},$$

where $z(s)$ is the coordinate of the sth molecule. The perturbation operator is a sum of pairwise terms

$$V_{st} = (-2z_s z_t + x_s x_t + y_s y_t)(e^2/z^3),$$

where the coordinates are local and z is along the line of centers between the sth and tth molecule.

The expectation value is

$$V = \nu^{-1} \int \sum_s e^{-ikz(s)} \psi_s{}^* \sum_{u<v} V_{uv} \sum_t e^{ikz(t)} \psi_t d\tau.$$

A particular V_{uv} mixes $\psi_u{}^*$ with ψ_v (and $\psi_v{}^*$ with ψ_u) giving the transition moment matrix elements of the u and v molecule as (vector) constants and requiring the inclusion of a factor $\mathbf{F}_{uv}$ which involves the distance apart and mutual orientation of the transition moment vectors. Thus, a typical term is

$$-\nu^{-1} e^{-ikz(s)} \mathbf{m}_s \mathbf{F}_{st} \mathbf{m}_t e^{ikz(t)}.$$

With appropriate qualification, we may replace the sum over s and t by an integral

$$V = -\nu^{-1}(\nu N/v) \int e^{-ikz'} \mathbf{m}(r') \mathbf{F}(r'r) \mathbf{m}(r) e^{ikz} d\tau d\tau'.$$

The factor N is the number of molecules per unit volume and is needed when the first sum is converted into the $d\tau$ integration (over all molecule like regions paired with one at r'). The factor $\nu/v(=N)$ is the total number of molecules divided by the total volume, which takes care of the $d\tau'$ part. This gives

$$V = -(N/v) \int e^{-ikz'} [\mathbf{m}(r') \mathbf{F}(r'r) \mathbf{m}(r) e^{ikz} d\tau] d\tau'.$$

Let us fix our attention on a molecule in the primed system at the origin, getting for the factor in brackets after the first integration the value

$$\int \mathbf{m}' \mathbf{F}(0,r) \mathbf{m} e^{ikz} d\tau.$$

Now we ask what value would be obtained for such an integral if the wave in the unprimed system were translated along the z axis,

$$e^{ikz} \longrightarrow e^{ik(z-\alpha)},$$

but also the plane in which the primed molecule in question lies were displaced: $r' \neq 0$, $z' = \alpha$. The value of the integral would naturally be unchanged ($\mathbf{m}$ values are constant in a plane normal to the propagation direction):

$$\int \mathbf{m}' \mathbf{F}(r'r) \mathbf{m} e^{ik(z-\alpha)} d\tau = \int \mathbf{m}' \mathbf{F}(0r) \mathbf{m} e^{ikz} d\tau,$$

but the integral on the left is at the same time

$$\int e^{-ikz'} \mathbf{m}' \mathbf{F}(r'r) \mathbf{m} e^{ikz} d\tau,$$

showing that the full integrand is always the same prior to the second integration over $d\tau'$ to give V. The matrix element is thus the volume v times the first integral taken, say, with respect to the origin,

$$V = -N \mathbf{m}' \int \mathbf{F}(0,r) \mathbf{m} e^{ikz} d\tau.$$

We may regard the transition moment $\mathbf{m}$ as a dipole moment, a point of view which leads us to define

$$\mathbf{P}(0) = \mathbf{m} N,$$

where $\mathbf{P}$ in the continuous case is treated like the classical polarization. This leads us to the result for V:

$$V = -\mathbf{m}' \int \mathbf{F}(r) \mathbf{P}(r) d\tau,$$

where

$$\mathbf{P}(r) = e^{ikz} \mathbf{P}(0).$$

This expression for V appears to be of the form

$$V = -\mathbf{m}' \cdot \mathbf{E}(0),$$

where $\mathbf{E}(0)$ is the field acting on a molecule at the origin owing to all the other molecules in the solid fictitiously polarized to give a polarization $\mathbf{P}$. We can now determine the function $\mathbf{F}(r)$ from the analogous function in classical electromagnetic theory.

The electric field may be derived from the Hertz vector

$$\mathbf{E} = (\text{graddiv} - \nabla^2) \mathbf{\Pi}.$$

The source of the Hertz vector is the polarization

$$\Box \mathbf{\Pi} = -4\pi \mathbf{P}.$$

Solving by means of the Green's function for retarded time, we have the contribution to $\mathbf{\Pi}$ from the polarization in $d\tau$ at s,

$$\mathbf{\Pi}(\mathbf{s}') = (e^{-ik_0|\mathbf{s}'-\mathbf{s}|} / |\mathbf{s}' - \mathbf{s}|) \mathbf{P}(\mathbf{s}) d\tau,$$

where $k_0=\omega/c$. The field at the origin due to a molecule at s is thus

$$\mathbf{E}(\mathbf{s}'=0)=(1/N)(\underset{\text{resp. } s'}{\text{graddiv}}-\nabla^2)\frac{e^{-ik_0|\mathbf{s}'-\mathbf{s}|}}{|\mathbf{s}'-\mathbf{s}|}\mathbf{P}(\mathbf{s})\Bigg|_{\mathbf{s}'=0},$$

where $1/N$ is the volume of a molecule. However, the field at the origin due to a dipole at $\mathbf{s}$ is the same as the field at $-\mathbf{s}$ caused by the same dipole $[\mathbf{P}(\mathbf{s})]$ moved to the origin. This latter quantity is

$$\mathbf{E}(\mathbf{r}'=-\mathbf{s})=(1/N)(\text{graddiv}-\nabla^2)\frac{e^{-ik_0|\mathbf{r}'-0|}}{|\mathbf{r}'-0|}\mathbf{P}(\mathbf{s})\Bigg|_{|\mathbf{r}'|=|\mathbf{s}|}.$$

Dropping the prime and remembering to use only the direction cosines of $\mathbf{P}$, we thus find

$$\mathbf{E}(0)=(1/N)(\text{graddiv}-\nabla^2)(e^{-ik_0r}/r)\mathbf{P}(\mathbf{r}),$$

which represents the electric field at the origin coming from an amount of polarization corresponding to a molecule at $\mathbf{r}$.

The foregoing is a classical result, so to be on the safe side we need to calibrate the expression by calculating just the static or Coulomb's law part. This can be carried out by omitting ∇^2 and using the graddiv part in conjunction with the Green's function without retardation $1/r$. This procedure leads to the static pairwise interaction provided that we connect the transition dipole with a fictitious classical polarization as described previously. We may therefore feel encouraged to calculate the radiation contribution by retaining the ∇^2 part and using the full Green's function. If all powers of r were retained, the calculation would automatically give the static contribution along with the radiation contribution. In the following, we retain only the long-range interaction, which is simpler; though eventually we go back to the consideration of the static interaction as well.

The procedure of using the full Green's function ostensibly eliminates the time from the calculation so that it is difficult to arrive at a physical interpretation (other than the classical one). What is implied is that the time factors occurring in a time-dependent expression for the expectation value are based on local time at the respective molecules and may not be neglected. Using the Green's function for retarded times in a sense freezes the phases of the molecules according to their distance from the origin, an effect which gives a spherical nodal pattern to be superimposed on the ordinary pattern of planar nodes belonging to the wave function.

We now calculate the contribution that comes from the radiation. The plan is to calculate the steady field at the origin that arises from the radiation and multiply it by $-\mathbf{m}'$. This vector is further assumed to point along the y axis.

The field at the origin is the sum of contributions from the molecules at $\mathbf{r}$, one such contribution being

$$(1/N)(\text{graddiv}-\nabla^2)(e^{-ik_0r}/r)\mathbf{P}(\mathbf{r})$$

or, considering that the propagation direction is z and the polarization y, the y component of the field is

$$m_yk_0^2(-\sin^2\phi+1)[(e^{-ik_0r}/r)+\cdots]e^{ikz(r)}.$$

The phase factor $e^{ikz(r)}$ is regarded here as a coefficient of one of the ψ's and is not differentiated. The graddiv part gives the term in $-\sin^2\phi$ together with terms which fall off as higher inverse powers of r, and these last are not retained.

Now, integrating over all molecules, we obtain

$$E_y(0)=m_yNk_0^2\int\frac{e^{-ik_0r}}{r}e^{ikr\cos\theta}\cos^2\theta r^2\sin\theta d\theta d\phi dr.$$

The integral gives rise to half-integral Bessel functions and the related Hankel functions[10]

$$j_n(\rho)=(\pi/2\rho)^{\frac{1}{2}}J_{n+\frac{1}{2}}(\rho),$$
$$h_n^{(2)}(\rho)=(\pi/2\rho)^{\frac{1}{2}}H_{n+\frac{1}{2}}(\rho).$$

The Green's function is

$$(k_0/i)h_0^{(2)}(k_0r),$$

and the plane wave

$$e^{i(kr)\cos\theta}=\sum_0^\infty(2\text{n}+1)(i)^nj_n(kr)\text{P}_n(\cos\theta).$$

The expression for the field becomes

$$-m_yNk_0^3i\int h_0^{(2)}(k_0r)$$

$$\sum^\infty(2\text{n}+1)(i)^nj_n(kr)\text{P}_n(\cos\theta)(\tfrac{1}{3}\text{P}_0+\tfrac{2}{3}\text{P}_2)r^2\sin\theta d\theta d\phi dr.$$

Integration over ϕ gives 2π and over θ gives $2(\frac{1}{3}j_0-\frac{2}{3}j_2)$, whence all together we have

$$-4\pi m_yNk_0^3i\int h_0^{(2)}(k_0r)[\tfrac{1}{3}j_0(kr)-\tfrac{2}{3}j_2(kr)]r^2dr.$$

By substituting

$$\text{Im }h_0^{(2)}=\cos k_0r/-ik_0r,\quad j_0(kr)=\sin kr/kr,$$

$$j_2(kr)=\frac{3\sin kr}{(kr)^3}-\frac{3\cos kr}{(kr)^2}-\frac{\sin kr}{kr},$$

and disregarding the terms (in j_2) which fall off faster than r^{-1}, this gives

$$4\pi m_yNk_0^3\int_a^A\frac{\cos k_0r}{k_0r}\frac{\sin kr}{kr}r^2dr,$$

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[10] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), Chap. VII.

where the limits are A, of macroscopic dimensions, and a, the radius of a small sphere surrounding the molecule or appropriate group of molecules at the origin. With $k=nk_0$, where n is a sort of index of refraction, and $\rho=k_0r$, this is

$$4\pi m_y N(1/n)\int_{k_0a}^{k_0A} \sin n\rho \cos\rho d\rho.$$

Evaluation gives

$$-4\pi m_y N(n^2-1)^{-1}[\cos nk_0A \cos k_0A-\cos nk_0a \cos k_0a + (1/n)(\sin nk_0A \sin k_0A-\sin nk_0a \sin k_0a)].$$

We have to know what to do about the contributions from the upper limit A. When $n<1$, the main contribution is from

$$(1/n)\sin nk_0A \sin k_0A.$$

When n is in the range of, say, $\frac{1}{10}$, the factor $1/(n^2-1)$ is sensibly -1, whereas the A contribution is not strongly divergent. Moreover, it oscillates markedly as A is changed ever so slightly ($k_0\sim 10^5$), an effect which is reminiscent of those found when the quantum theory is used to describe the macroscopic part of a measurement.[11] For this reason we may replace the oscillating term by its average, which is zero. Probably this zero value would be found if we were to employ standing waves with coefficients c_s going to zero at the surfaces in place of the infinite running waves with coefficients $e^{ikz(s)}$. Although the situation is not wholly satisfactory, we take as our result the field obtained by ignoring the surface effect and by assuming that a is of molecular dimensions ($a\sim 10^{-7}$ cm), whence $k_0a\sim 0$. This gives a steady field at the origin,

$$4\pi m_y N(n^2-1)^{-1},$$

and a corresponding energy which is designated as V_3,

$$V_3=-4\pi m_y^2 N\cdot(n^2-1)^{-1}.$$

This result must be understood as applying only at the low ($n=\infty$) and high ($n=0$) frequency boundaries of the region of total reflection. Outside this region, the polarization amplitude falls off from the "resonance" value of m_yN and the incident light passes through the crystal (only to be extinguished by the surface charges). Inside the region there is a second branch, so to speak, of the field in its dependence on n; but always with damping, which is not explicitly included here. For example, when $n\rightarrow 1 (k\rightarrow k_0)$, the field is represented as approaching $\pm\infty$ asymptotically, but with the damping, the radiation correction at this point is very likely zero.

In the full calculation of the perturbation energy, combining the static contribution with the radiation correction, the final result consists of two parts in addition to V_3: a short-range static part V_1; and a long-range static part V_2.

The short-range part may be calculated by summing out to a distance of ten intermolecular distances or so in all directions from the origin. It corresponds to the calculation of the Davydov energy with strong coupling. Practically, it is almost independent of k_0 and n, if these quantities stay in the range corresponding to the experiments being described herein. Calculation of the short-range part leads to a frequency

$$\omega_0=\omega+V_1/\hbar.$$

The collection of molecules having ω_0 as the frequency is small enough to be considered a "single molecule" in the evaluation of the radiation part V_3; so probably ω_0 is the correct frequency to use for k_0 in the Green's function.

The long-range static part is difficult to calculate as an integral using a procedure analogous to the one preceding for the radiation part. However, this has been done for $n=0$ assuming the material is contained in an infinite rectangular slab bounded by two xz planes at different y values.[12] The field at a single molecule turns out to be $-(8/3)\pi N m_y$. The free charges on the xz plane surfaces give a contribution $-4\pi N m_y$, and if we wish not to count this for reasons similar to the ones discussed previously, we have to add $4\pi N m_y$ (this is similar to adding $4\pi\mathbf{P}$ to $\mathbf{E}$ to give $\mathbf{D}$). What remains is the internal field

$$E_{0y}=\tfrac{1}{3}4\pi m_y N,$$

leading to a red shift

$$V_2=-\tfrac{1}{3}4\pi m_y^2 N.$$

Incorporating V_1, V_2, and V_3, we have the result (valid at $n=0$ and $n=\infty$ only)

$$V=V_1-4\pi m_y^2 N[\tfrac{1}{3}+(n^2-1)^{-1}]$$

or

$$V-V_1=-\tfrac{4}{3}\pi m_y^2 N[(n^2+2)/(n^2-1)]=V_2+V_3.$$

To round out the argument we should need to see whether the result for V_2 holds in the case where retardation is considered and n is allowed to be different from zero. The classical theory of dispersion presented in Rosenfeld[13] shows that in the dielectric (as opposed to absorptive) region, apart from surface effects and for a cubic crystal,

$$E_{0y}=\tfrac{4}{3}\pi P_{0y}[(n^2+2)/(n^2-1)]$$

[Eq. (30)]. If we make the substitution $P_{0y}=Nm_y$, we in effect obtain the result given previously for V_2+V_3 at the boundaries of the absorptive and dielectric regions, but now through a derivation including variable n and retardation. The comparison establishes the equivalence between the quantum theory and the dis-

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[11] D. Bohm, *Quantum Theory* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1951), Chap. 22.

[12] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, New York, 1955), second edition, Chap. XII; B. R. A. Nijboer and F. W. deWette, Physica **24**, 422 (1958).

[13] L. Rosenfeld, *Theory of Electrons* (Interscience Publishers, Inc., New York, 1951), Chap. VI.

persion theory used earlier, and in particular shows that the explicit resonance ω_0 already has to involve V_1. The entire treatment could be shortened by going directly to Rosenfeld's Eq. (30), but perhaps at the cost of some understanding.

We now consider V_2 and V_3 as providing the explanation of the bounding frequencies ω_- and ω_+. In case $n=\infty$ ($\lambda=0$), the phases of the oscillating dipoles in succeeding planes of the crystal, normal to k, change sign. This gives no radiation correction owing to rapid cancellations ($V_3=0$ if $n=\infty$), but the conventional electrostatic level shift has to be supplemented by a red shift attributable to the static internal field. This tives an interpretation of ω_- as involving V_2 only:

$$\hbar(\omega_- - \omega_0) = -\tfrac{4}{3}\pi m_y{}^2 N.$$

For BDP, the low-frequency boundary of metallic reflection comes at 470 mμ, whereas the Davydov energy shift gives ω_0 corresponding to 340–350 mμ, well to the blue of the single-molecule band at 409 mμ.

When $n=0$ ($\lambda=\infty$), the phases of the oscillating dipoles are all the same, and the contribution to the energy from the radiation overweights the internal field part, $V_3+V_2>0$, giving a net blue shift

$$\hbar(\omega_+ - \omega_0) = +(8\pi/3) m_y{}^2 N.$$

The reflection edge in BDP corresponding to ω_+ is at 310 mμ, in qualitative agreement. The preceding formulas are not in quantitative agreement with the experimental ω values because ω_0 was obtained as a derived quantity from the classical dispersion theory including the G term as representing the higher transitions. The difference $\hbar(\omega_+ - \omega_-)$, where ω_+ and ω_- are as defined in the foregoing is $4\pi m_y{}^2 N$, the same as found in the Sec. IV using $G=0$ and the dispersion theory.

The picture which emerges[9] is very different from the conventional one (for example, Fig. 2 of reference 8 is incorrect). In the conventional picture, the vacuum **E** and **B** vectors pervade the solid, interacting with a single allowed crystal level which has almost an infinite wavelength, and the energy of which is determined by considering the short-range static interaction. The k vector is supposed to coincide with the k vector of the light and simultaneously correspond to a frequency $\Delta E/h$, where ΔE is the crystal transition energy.

In the present picture when $\omega_p{}^2 > 2m\omega_0$, we imagine that there are an infinite number of allowed transitions, with k going from 0 to ∞ on the frequency boundaries. The states reached in these transitions are themselves lightlike, and as intermediate states are responsible for the dispersion phenomenon. In the metallic reflection region, the light excites a physical block of material by interacting with the plane of incidence (to a certain depth depending on γ) and all frequencies of the light from one frequency boundary of the metallic reflection region to the other are effective.

By not including the damping, we have left the nature of the crystal levels uncertain. The question has even been asked whether they can be considered as stationary states.[14] Low-temperature measurements directed towards answering this and related questions are currently being undertaken.

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[14] C. A. Mead, Phys. Rev. **110**, 359 (1958).